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ABSTRACT

A new methodology for calculating high temperature and pressure elastic moduli in metals has been developed accounting for both the electron-thermal and ion-thermal contributions. Anharmonic and quasi-harmonic thermoelasticity for bcc tantalum have thereby been calculated and compared as a function of temperature (<12,000 K) and pressure (<10 Mbar). In this approach, the full potential linear muffin-tin orbital (FP-LMTO) method for the cold and electron-thermal contributions is closely coupled with ion-thermal contributions obtained via multi-ion, quantum-based interatomic potentials derived from model generalized pseudopotential theory (MGPT). For the later contributions two separate approaches are used. In one approach, the quasi-harmonic ion-thermal contribution is obtained through a Brillouin zone sum of the strain derivatives of the phonons, and in the other the anharmonic ion-thermal contribution is obtained directly through Monte Carlo (MC) canonical distribution averages of strain derivatives on the multi-ion potentials themselves. The resulting elastic moduli compare well in each method and to available ultrasonic measurements and diamond-anvil-cell compression experiments indicating minimal anharmonic effects in bcc tantalum over the considered pressure range.

Existing methods to calculate the thermoelastic moduli for a single crystal material include, for example, molecular dynamics[1] and Monte Carlo techniques[2] where only the ionic contribution is calculated, or the particle-in-a-cell method[3] where both electronic and ionic contributions (treated only approximately) are calculated. We present here a new methodology for calculating the high temperature and pressure elastic moduli that separates the Helmholtz free energy into cold, electronic and ionic contributions and makes a full calculation for each component. Two methods of calculating the ion-thermal contributions are presented and compared: one within the quasi-harmonic phonon approximation and the other being fully anharmonic. Both ion-thermal treatments produce similar results in the case of Ta indicating negligible anharmonic effects for the high pressure phase diagram for this metal.

For high temperatures (300 K $\leq$ T $\leq$ T$_{melt}$) and pressures (P< 10 Mbar), we assume that the electron-phonon coupling is negligible for a metal and write the Helmholtz free energy as, $F(\Omega,T) = \Phi_o(\Omega,T=0) + F_e(\Omega,T) + F_H(\Omega,T) + F_A(\Omega,T)$, where $\Phi_o(\Omega,T=0)$ is the total energy of the electronic ground state, i.e. the frozen lattice, $F_e(\Omega,T)$ contains the electron-thermal contribution, $F_H(\Omega,T)$ holds the ion-thermal contribution, and $F_A(\Omega,T)$ has the anharmonic contributions. The specific volume Ω is the volume per atom. With this and through the definition of the isothermal elastic moduli $C^T_{ijkl} = \Omega^{-1}\partial^2 F/\partial\eta_{ij}\partial\eta_{kl}\mid_{T\eta'}$, where η' indicates that all other strains are held fixed, the individual contributions to the elastic moduli are obtained, $C^T_{ijkl} = C^o_{ijkl} + C^e_{ijkl} + C^{ion}_{ijkl}$. For the C^e_{ijkl} term, temperature is incorporated into $F_e(\Omega,T) = U_e - TS_e$ through a broadening of the electron density of states, $n(\epsilon,\Omega)$, via the Fermi-Dirac distribution, $f(\epsilon)$, and through the electronic entropy, $S_e(\Omega,T) = -k_B \int d\epsilon\, n(\epsilon,\Omega)\{f(\epsilon)ln[f(\epsilon)] - (1-f(\epsilon))ln[1-f(\epsilon)]\}$. To calculate this term, the full-potential, linear muffin-tin orbital(FP-LMTO) electronic-structure method is used [4].

For the C_{ijkl}^{ion} contribution, we have implemented two different calculations to assess the anharmonic contribution: one within the quasi-harmonic(QH) approximation and one that is fully anharmonic(AH). Specifically for the QH method, following Wallace [5], the Helmholtz free energy for the lattice is written as a Brillouin zone and branch(κ) sum of the phonon frequencies ω_κ as $F_{ion} = \sum_\kappa 0.5\hbar\omega_\kappa + ln[1 - exp(-\hbar\omega_\kappa/kT)]$. Therefore, to obtain C_{ijkl}^{ion}, strain derivatives of F_{ion} lead to a summation over the Brillouin zone of strain derivatives of the phonon frequencies. To compute the fully AH lattice contribution to the elastic moduli, we have extended previous MC work[2], where the strain derivatives of the partition function are taken while accounting for periodic boundary conditions. This leads to a canonical assemble average of these derivatives evaluated at thermodynamic equilibrium for a given Ω and T via a standard Metropolis, MC algorithm. Two to three runs for each Ω and T point were performed with a run lasting at least 1.5×10^6 MC-steps. In both ion-thermal methods, we have used a quantum derived, multi-ion potential for Ta from the model generalized pseudopotential theory(MGPT) [6].

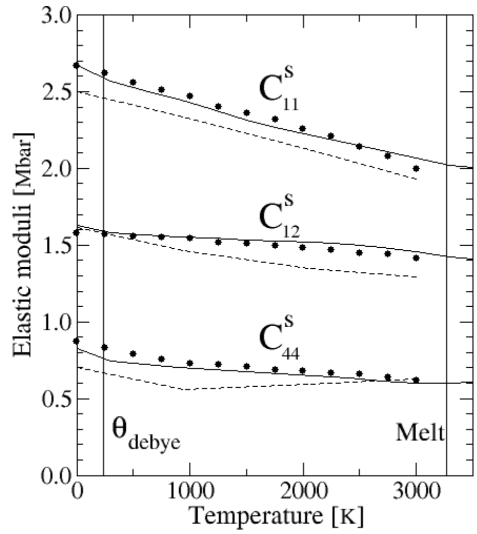

Fig. 1: The thermal dependence of the calculated C_{ijkl}^S (solid line) at ambient pressure up to T$_m$= 3376 K is compared to experiment[7] (circle). The dashed lines are from Gülseren and Cohen's work [3].

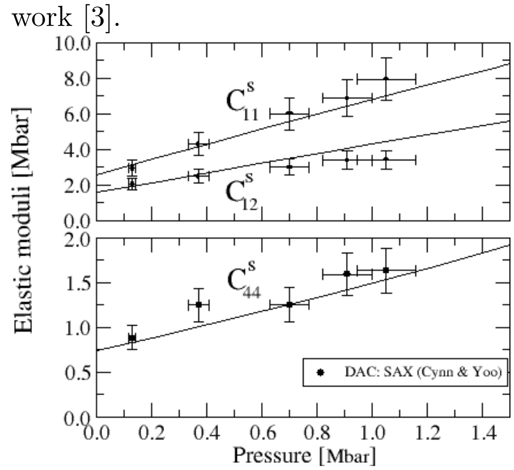

Fig. 2: The calculated C_{ijkl} (line) at T=300 K captures the pressure dependence as compared to SAX-DAC data[8](circle).

We first compare the calculated adiabatic moduli C_{ijkl}^S obtained from $C_{ijkl}^T(\Omega,T)$ with electronic plus QH thermal contributions against experimental data, Figs.(1 and 2). We have found that it is necessary to include both the electron- and ion-thermal components of the C_{ijkl}, since each is of similar magnitude, roughly 0.1 Mbar at T= 2500 K and P= 0. Since the electron thermal plus QH ion-thermal calculation describe well the available experimental values, we now compare only the computation of $C_{ijkl}^{ion}(\Omega,T)$ by the QH and AH calculations. Overall the AH calculation yields similar values compared to the QH calculation, especially below 1 Mbar and even near T_m. As the pressure increases, the AH calculated values deviate from the QH values at temperatures just below T_m(see Fig. 3). At pressures above 6 Mbar, the AH calculated values only begin to deviate from the QH calculation within 80% of the T_m. This indicates that Ta has negligible anharmonic effects (deviation from high temperature, linear dependence) over a broad range of pressure with temperature nearing T_m. This linear temperature dependence of the C^T_{ijkl} leads to linear dependence in Voigt averaged shear modulus, albeit the pressure dependence of the cold shear modulus is non-linear above 6 Mbar.

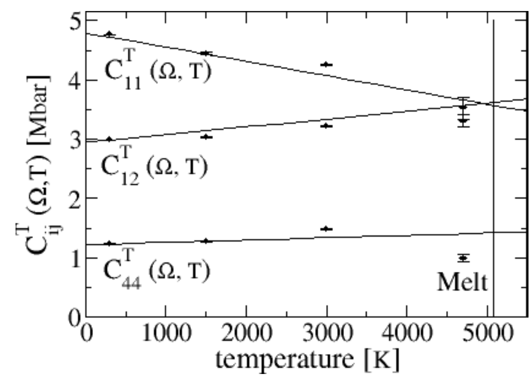

Fig. 3: The QH (line) and AH (circle) calculations of the $C^{ion}_{ijkl}(\Omega, T)$ term at Ω =102.2 a.u.^{3} for Ta. The pressure varies from 0.5 to 0.7 Mbar nearing T_m = 5074 K.

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References

[1] R. J. Wolf, K. A. Mansour, M. W. Lee and J. R. Ray, *Temperature dependence of elastic constants of embedded-atom models of palladium*, Phys. Rev. B **46**, 8027 (1992).

[2] C. W. Greeff and J. A. Moriarty, *Ab initio thermoelasticity of magnesium*, Phys. Rev. B **59**, 3427 (1999).

[3] O. Gülseren and R. E. Cohen, *High-pressure thermoelasticity of body-centered-cubic tantalum*, Phys. Rev. B **65**, 064103 (2002).

[4] P. Söderlind and J. A. Moriarty, *First-principles theory of Ta up to 10 Mbar pressure: Structural and mechanical properties*, Phys. Rev. B **57**, 10340 (1998).

[5] D. C. Wallace, *Thermodynamics of crystals*, Dover: Mineola, NY (1998).

[6] J. A. Moriarty, et al. *Quantum-based atomistic simulation of materials properties in transition metals*, J. Phys.: Cond. Mat. **14**, 2825 (2002).

[7] E. Walker and P. Bujard, *Anomalous temperature behavior of the shear elastic constant C_{44} in tantalum*, Solid State Comm. **34**, 691 (1980).

[8] H. Cynn and C.-S. Yoo, *Single crystal elastic constants of tantalum to 105 GPa*, LLNL internal document UCRL-JC-137930 (unpublished).